



## Radiation induced degradation of antiepileptic drug primidone in aqueous solution



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### HIGHLIGHTS

- Electron beam irradiation was efficient for removal of primidone in aqueous solution.
- The degradation kinetics of primidone conformed to pseudo-first-order equation.
- Hydroxyl radical was shown to be the most reactive species in primidone radiolysis.
- Possible pathways of primidone degradation were proposed.

### ARTICLE INFO

#### Article history:

Received 16 October 2014

Received in revised form 26 January 2015

Accepted 29 January 2015

Available online 8 February 2015

#### Keywords:

Primidone (PMD)

Hydroxyl radical

Advanced oxidation processes

Electron beam irradiation

### ABSTRACT

The present study was to determine the effectiveness of electron beam irradiation for degradation of the antiepileptic drug primidone (PMD) in aqueous solution. The results showed that PMD degradation followed pseudo-first-order kinetics. The dose constant determined in this study ranged from 1.26 to 4.59 kGy<sup>-1</sup>, and decreased with an increase in the PMD initial concentration, whereas the initial radiation chemical yield for the loss of PMD decreased with increasing of absorbed dose and increased as the PMD concentration increased. The effects of medium pH, the presence of SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> anions, H<sub>2</sub>O<sub>2</sub>, iso-propanol, and saturated solutions of N<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>O were also investigated. The results demonstrated that the ·OH took the most important role in the degradation of PMD, while the reductive e<sub>aq</sub><sup>-</sup> and ·H took the less important role in PMD degradation. Major degradation products of PMD, including degradation intermediates, low weight organic acids and some inorganic ions were detected by LC/MS/MS and IC. Formic acid, acetic acid, oxalic acid, maleic acid and NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> were identified in the irradiated solutions. Possible pathways for PMD decomposition by electron beam irradiation in aqueous solution were proposed.

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### 1. Introduction

Due to the unknown environment impact and possible damages to the flora and fauna in aquatic systems, pharmaceutical contaminants in the environment have raised much attention [1,2]. Pharmaceuticals are capable of passing through cellular membranes and avoiding the deactivation in the body to have their desired physiological effect [3]. Over the past decades, pharmaceuticals have been increasingly manufactured and consumed. At the present, there are over 4000 active substances that are available in the market as pharmaceuticals [4]. However, most of the

pharmaceuticals are not completely degraded after application [5]. Thus, some unchanged forms and the metabolites of the pharmaceuticals enter the ecosystem after being excreted. Certain chemically and biochemically-persistent pharmaceuticals have been frequently detected in surface water [6–9], drinking water [10,11], wastewater [12,13] and sediments [14].

Antiepileptic drugs are designed to control seizures in the management of epilepsy [15]. Primidone (PMD) is a first-generation antiepileptic drug. It is a water-insoluble deoxyphenobarbital, which was introduced to the clinics in 1952 [16]. Up to date, the occurrence and fate of PMD in the environment has been studied by many researchers [17–21]. Although the concentrations of PMD are low in the environment, which range up to several hundreds of ng L<sup>-1</sup> [21,22], they may present a potential hazard for human health.

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Under this situation, advanced oxidation processes (AOPs) for removal of PMD have been developed, such as UV [23], photo-Fenton [24], UV/H<sub>2</sub>O<sub>2</sub> [25]. However, the degradation efficiency of PMD by these processes was low. Ionizing radiation, as an AOP, has been widely used for the degradation of stable organic pollutants. For example, Wu et al. [26,27] studied and found that the electron beam radiolysis was an effective method to degrade phthalate aqueous solution. Iamail et al. [28] investigated the degradation of chlorpyrifos by gamma irradiation and demonstrated that the oxidative ·OH radicals are the most important species during the process. Moreover, pollutants can be degraded in most cases to less toxic and in some cases to more biodegradable compounds by ionizing irradiation. Finally, the organic pollutants can be converted to carbon dioxide and water [29,30]. However, at present, the economic feasibility of this method is often not acceptable. Thus, it is necessary to obtain fundamental data on the degradation efficiency and the by-products to evaluate the application of AOPs.

This study focused on PMD degradation using electron beam radiation as means to investigate the applicability of AOPs for the destruction of PMD. The aims of this study were to: (1) investigate the electron beam irradiation degradation of PMD solution in aqueous media, (2) investigate the PMD degradation kinetics and effect of initial concentration on degradation process, (3) evaluate the effects of various radical scavengers and promoters on the degradation of PMD by electron beam irradiation, (4) identify the main intermediates, organic acids and ions that were produced during irradiation process and propose the possible pathways of PMD degradation in aqueous solution.

## 2. Experimental

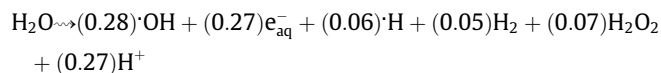
### 2.1. Materials

PMD was purchased from ICN pharmaceuticals with >98% purity. HPLC grade acetonitrile was obtained from Sigma–Aldrich. All of the chemical reagents used (sodium sulfite, sodium sulfate, sodium nitrite, sodium nitrate, sodium carbonate, sodium bicarbonate, sodium chloride, ammonium chloride, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, w/w) and iso-propanol) were of analytic grade and purchased from Shanghai Chemical Reagent Co. Ltd. The pH of the solution was adjusted using sodium hydroxide or sulfuric acid where needed. A Milli-Q water purification system from Millipore (Sartorius 611, Germany) was used throughout the study to obtain HPLC-grade water. High purity N<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>O (99.999% purity) were used.

### 2.2. Irradiation process

All irradiation experiments were conducted using electron accelerator (GJ-2-II, Xianfeng electrical plant) with beam energy of 1.8 MeV and variable current (0–10 mA), which belonged to Institute of Applied Radiation, Shanghai University, China. The dose rate of 0.045 kGy s<sup>-1</sup> was utilized. Aqueous PMD solutions were irradiated at different doses and all experiments were performed at room temperature (20 ± 2 °C).

Electron beam irradiation of aqueous media results in the formation of three main reactive species, e<sub>aq</sub><sup>-</sup>, ·OH, and ·H, and less reactive species (reaction 1) [31]:



where, the values in square brackets are radiation yield (*G*-value) of each species in μmol J<sup>-1</sup> absorbed energy. The three main reactive

species can react with each other or with other solutes present in the solution [31].

### 2.3. Analytical procedures

PMD concentration in aqueous solution was determined by reversed phase high performance liquid chromatography (HPLC) using a liquid chromatography (Agilent 1200, USA) equipped with a VWD detector and an autosampler. The chromatographic column was a C<sub>18</sub> (150 mm × 4.6 mm × 5 μm) reversed phase column. The mobile phase was a mixture of ultrapure water and acetonitrile (60/40, v/v) at flow rate of 0.8 mL min<sup>-1</sup>; Detector wavelength was 225 nm; and injection volume was 10 μL.

The organic acids and ions produced from PMD by electron beam irradiation were analyzed by ion chromatography (Dionex ICS1100). The determination was achieved on hydrophilic anion exchange column. For anions determination, the standard eluent was mixed with 4.5 mM Na<sub>2</sub>CO<sub>3</sub> and 1.4 mM NaHCO<sub>3</sub> at a flow rate of 1.2 mL min<sup>-1</sup>. The injection volume was 25 μL. For cation determination, the eluent was 20 mM methanesulphonic acid. The flow rate was 1 mL min<sup>-1</sup> and the injection was 25 μL.

Intermediate identification was carried out with HPLC (Agilent 1260) coupled with Triple Quad MS (Agilent 6460) using ESI+ ionization, and operating in full-scan mode. Separation was carried out using a C<sub>18</sub> (100 mm × 3.0 mm × 2.7 μm) column at a flow rate of 0.4 mL/min. Mobile phase was a mixture of acetonitrile and water (v:v = 25:75).

## 3. Results and discussion

### 3.1. Determination of dose constant and kinetic study

The degradation of PMD at four different concentrations from 25 to 100 mg L<sup>-1</sup> by electron beam radiolysis was studied. As exhibited in Fig. 1, the PMD could be effectively degraded under low dose of irradiation. For example, PMD in aqueous solution was completely degraded at 2 and 3 kGy when the initial concentration was 25 and 50 mg L<sup>-1</sup>, respectively. However, at given concentration, the rate of PMD degradation percentage change decreased with increased absorbed dose and at a given dose, the degradation was more efficient at lower concentration than that at higher concentration. This can be explained that PMD has a high

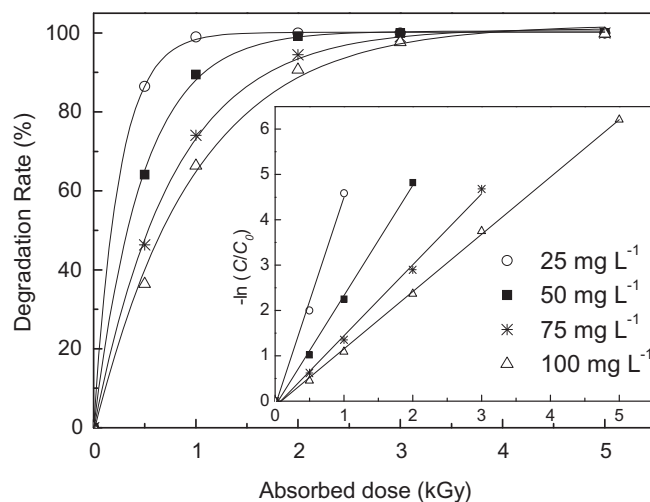


Fig. 1. Removal of PMD at different initial concentrations with increasing dose (Inset: determination of dose constant for the radiolysis of PMD at different concentrations.)

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